

Absence of simulation evidence for critical depletion in slit-pores

Nigel B. Wilding

*Department of Physics and Astronomy, The University of Edinburgh,
Edinburgh EH9 3JZ, U.K.*

Martin Schoen

*Fachbereich Physik–Theoretische Physik, Bergische Universität Wuppertal,
Gaußstrasse 20, D-42097 Wuppertal, Germany*

Recent Monte Carlo simulation studies of a Lennard-Jones fluid confined to a mesoscopic slit-pore have reported evidence for “critical depletion” in the pore local number density near the liquid-vapour critical point. In this note we demonstrate that the observed depletion effect is in fact a simulation artifact arising from small systematic errors associated with the use of long range corrections for the potential truncation. Owing to the large near-critical compressibility, these errors lead to significant changes in the pore local number density. We suggest ways of avoiding similar problems in future studies of confined fluids.

I. INTRODUCTION

In recent papers [1–3], one of us has reported grand canonical Monte Carlo simulation studies of a Lennard-Jones fluid confined between two structureless attractive walls arranged in a slit-pore geometry. The behaviour of the number density profile across the pore, $\rho(z)$, was studied for various values of the thermodynamic parameters, namely the chemical potential, μ , and temperature, T . At certain values of μ and T (apparently close to those of the bulk liquid-vapour critical point) it was observed that the average local density in the middle of the pore fell markedly below the value obtained in a fully periodic simulation performed at the *same* μ and T . These findings were used to argue in favour of the existence of a generic “critical depletion” phenomenon, namely the proposed tendency of a critical fluid to be expelled by a confining medium, even when the confining walls strongly attract the fluid particles [2]. Such a scenario is supported by experimental findings for SF₆ adsorbed in mesoporous materials [3,4], for which a dramatic reduction in adsorption was observed as the bulk critical temperature was approached from above along the critical isochore.

In this note we point out that the apparent critical depletion reported in references [1–3] is actually a simulation artifact arising from systematic errors associated with the corrections applied to the configurational energy to compensate for the truncation of the interparticle potential. Using new simulations, we show that if one chooses a sufficiently large truncation distance or alternatively avoids the use of truncation corrections altogether, then the depletion effect disappears.

II. SIMULATION DETAILS AND RESULTS

The simulation arrangement and procedure employed in this work are the same as those described in refs. [1,2], and accordingly we merely summarise the principal features.

Grand canonical Monte Carlo simulations [5] were performed for a Lennard-Jones fluid, having an interparticle potential of the form:

$$U_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (2.1)$$

where ϵ and σ are respectively the Lennard-Jones well depth and scale parameters. Two distinct geometries were studied:

1. A fully periodic system.
2. A slit-pore geometry, in which the fluid is confined between two parallel structureless walls, having periodic boundary conditions in the directions parallel to the walls.

In the latter case, the walls were taken to exert a potential on the fluid particles of the form:

$$U_{FW} = 4\epsilon f \left[\frac{2}{5} \left(\frac{\sigma}{z} \right)^{10} - \left(\frac{\sigma}{z} \right)^4 \right], \quad (2.2)$$

where f is a parameter that tunes the strength of the wall-fluid interactions relative to those of the fluid interparticle interactions.

As in the previous studies of this system [1,2], the reduced temperature was set to the value $T = 1.36$, believed to be close to the bulk critical temperature. The chemical potential μ of the periodic system was then tuned until the equilibrium density reached the value $\rho = 0.365$, believed to be close to the bulk critical density. The resulting value of μ was then fed into a simulation of the slit-pore system at the same temperature and with the choice $f = 0.9836$. In both the periodic and slit-pore arrangements, the Lennard-Jones interparticle potential was truncated at some radius and a compensating correction applied to the configurational energy. For the periodic system, this correction was calculated in the standard fashion by assuming a spherical cutoff surface of radius r_c centred on each particle, combined with a uniform density approximation (UDA) for $r > r_c$. This yields for the energy correction per particle:

$$u_{pbc} = \frac{1}{2} 4\pi\rho \int_{r_c}^{\infty} dr r^2 U_{LJ}(r) = \frac{8}{3} \pi \rho \epsilon \sigma^3 \left[\frac{1}{3} \left(\frac{\sigma}{r_c} \right)^9 - \left(\frac{\sigma}{r_c} \right)^3 \right], \quad (2.3)$$

where $\rho = \langle N \rangle / V$ is the average number density of the system.

In the case of the slit-pore system, the truncation correction used was that given by Schoen et al. [6], which assumes a cylindrical cutoff surface (on whose principal axis each particle lies) extending across the whole width D of the pore, i.e. such that the cylinder ends coincide with the pore walls. This yields

$$u_{pore} = -\frac{\pi \epsilon \sigma^6}{s_c^3} \tan^{-1} \left(\frac{D}{s_c} \right) V \rho^2, \quad (2.4)$$

where s_c is the radius of the cutoff cylinder.

We have studied the effect of the cylindrical cutoff radius s_c on the density profile $\rho(z)$ of the slit-pore system. For each choice of s_c , the μ value employed in the simulation was that yielding an average density $\rho = 0.365$ in a periodic system of the same dimensions and with $r_c = s_c$. For small cylindrical cutoffs ($s_c = 3.5\sigma$), figure 1 shows that the local density in the pore middle is depleted with respect to the density of the periodic system (dashed line) at the same T, μ . This is the result reported in refs. [1–3]. However, new results for a larger choice of the cylindrical cutoff (also included in figure 1) show that this depletion reduces as s_c is increased, and in fact vanishes for $s_c \gtrsim 5.0\sigma$. This dependence of the depletion on the choice of s_c was missed in the previous studies [1,3].

We have also performed simulations in which we dispense with the use of cutoff corrections altogether and simply simulate a system of particles interacting via a truncated Lennard-Jones potential. The results (figure 2), exhibit no sign of a density depletion in the pore middle with respect to the periodic system.

III. DISCUSSION AND CONCLUSIONS

The dependence of the density depletion on the choice of the cylindrical cutoff s_c (figure 1) points to a breakdown of the uniform density approximation invoked in the derivation of the truncation correction for the internal energy, eq. 2.4. This approximation assumes that the number density outwith the cutoff surface is uniform, having the average system density $\rho = \langle N \rangle / V$. However, figures 1 and 2 show that for a slit system, $\rho(z)$ exhibits considerable structure across the pore, especially close to the walls. Accordingly, one must expect some measure of systematic error to be associated with eq. 2.4. Tests show that for the choice of cutoff $s_c = 3.5\sigma$ employed in references [1–3], this error is very small, so that in most circumstances eq. 2.4 represents a good approximation.

It seems, however, that in the critical region, even a very small error in the truncation correction can lead to large effects on the local pore number density. The reason for this is the large near-critical compressibility, reflected in the fact that near T_c , isotherms of $\mu(\rho)$ become very flat (see eg. figure 3 of [2]). Since the error in the truncation correction acts rather like a shift in the bulk (chemical potential) field with respect to the periodic system, large alterations to the local pore density may result. This is in accord with the observation [1,3] that the depletion is large close to the critical point, but diminishes as one moves to higher temperatures along the critical isochore.

To avoid similar problems arising in future studies of the effects of confinement on near critical fluids, it would seem wise to adopt one of the following strategies:

1. Employ a very large value for the truncation range and test for any systematic dependence of results on its value. This is clearly a very computationally intensive solution.
2. Employ a truncated potential and dispense with corrections altogether. Such a system is clearly well defined but causes complications if one wishes to model real substances.
3. Employ a cut and shifted potential which tends smoothly to zero at the cutoff.

In summary, we have demonstrated that the apparent critical depletion reported in [1–3] was actually an artifact arising from systematic errors in the energy correction for the tail truncation in the slit-pore geometry. Although numerically small, these errors can (in the critical region) strongly influence the fluid local number density of the confined system compared to a periodic system at the same temperature and chemical potential. Thus our findings underline the care that must be taken when implementing any sort of truncation corrections for near critical fluid models.

Further simulation studies of the near-critical properties of a confined fluid are in progress and a detailed account of these and their implications for theory and experiment on critical depletion will be presented in a later paper.

ACKNOWLEDGMENTS

NBW is grateful to R. Evans and A. Maciolek for stimulating his interest in critical depletion, and for most useful correspondence. He also thanks the Royal Society (grant number 19076), the Royal Society of Edinburgh and the EPSRC (grant no. GR/L91412) for financial support. MS is grateful to G.H. Findenegg for discussions and acknowledges financial support from the Sonderforschungsbereich 448 “Mesoskopisch strukturierte Verbundsysteme”

-
- [1] M. Schoen and M. Thommes, Phys. Rev. E **52**, 6375 (1995).
 - [2] M. Schoen, M. Thommes, G.H. Findenegg, J. Chem. Phys. **107**, 3262 (1997).
 - [3] M. Thommes, G.H. Findenegg and M. Schoen, Langmuir **11**, 2137 (1995).
 - [4] M. Thommes, G.H. Findenegg, H Lewandowski, Ber. Bunsenges. Phys. Chem. **98**, 477 (1994).
 - [5] D. Frenkel and B. Smit, *Understanding Molecular Simulation*, Academic Press, Boston, (1996).
 - [6] M. Schoen, D.J. Diestler and J.H. Cushman, J. Chem. Phys. **87**, 5464 (1987).

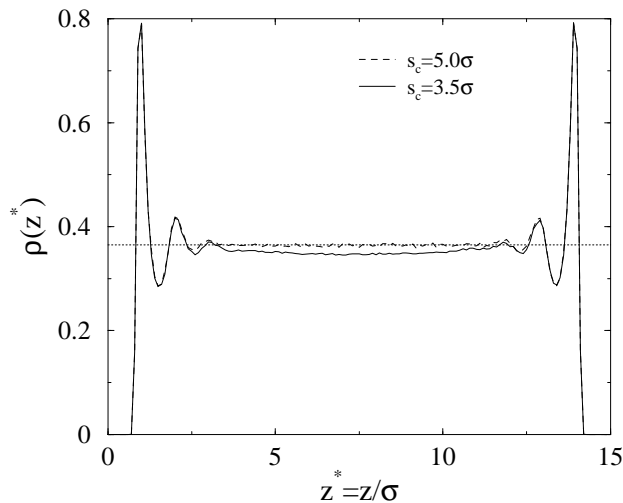


FIG. 1. The number density profile $\rho(z)$ (corresponding to a slit-pore of width $D = 15\sigma$) at two values of the cylindrical cutoff radius. In each case, the reduced temperature is $T = 1.36$ and the chemical potential μ used is that which yields an average density $\rho = 0.365$ (horizontal line) in a periodic system of linear size $L = 15\sigma^3$ at the same T . The figure shows that as the cylindrical cutoff radius is increased, the depletion disappears.

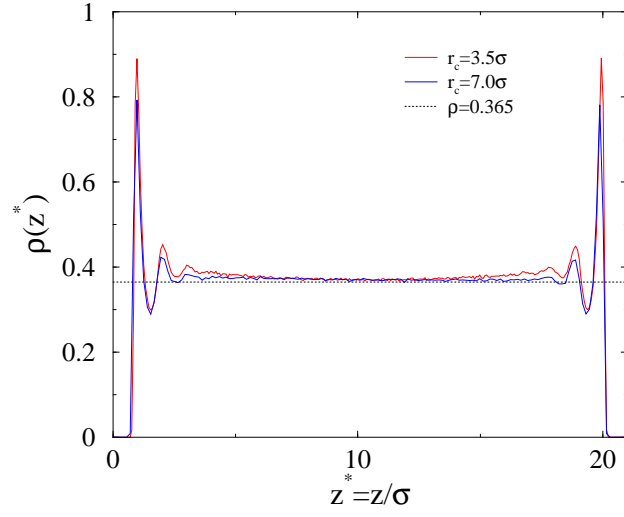


FIG. 2. The number density profile $\rho(z)$ (corresponding to a slit-pore of width $D = 21\sigma$) for a truncated potential with no tail correction applied. In each case the reduced temperature is $T = 1.36$ and the chemical potential μ used is that which yields an average density $\rho = 0.365$ (horizontal line) in a periodic system of linear size $L = 21\sigma^3$ at the same T .